<International Research Center for Elements Science> Organotransition Metal Chemistry

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Scope of Research

This laboratory aims at establishment of new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using experimental methods such as kinetic techniques as well as theoretical methods. The research subjects include: (1) development of novel organotransition metal systems for catalysis based on precise ligand design, (2) preparation of π-conjugated polymers by the use of well defined cross-coupling reactions, and (3) development of functional molecules including redox-active transition-metal clusters.

Research Activities (Year 2008)

Presentations

Catalytic Applications of Transition Metal Complexes Bearing Diphosphinidenecyclobutenes (DPCB-Y), Ozawa F, International Symposium on Chemistry Concerto Catalysis Based on Synergy of Elements, 12 July 2008, Rennes, France (Invited).

Electron-Induced Dynamic Behavior of [4Fe–4C] Cluster Core, Okazaki M, Takano M, Yoshimura K, Ozawa F, 38th International Conference on Coordination Chemistry, 24 July 2008, Jerusalem, Israel.

Grants

Ozawa F, Okazaki M, Takita R, Nakajima Y, Synergistic Effects of Transition Metals and Heavier Main Group Elements in Functional Organometallic Complexes, Grant-in-Aid for Priority Areas "Synergy of Elements", 1 September 2006–31 March 2010.

Ozawa F, Takita R, Nakajima, Y, Studies of Cross-coupling Reactions for Precise Synthesis of π- Conjugated Polymers, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2008–31 March 2010.

Okazaki M, Mihara H, Construction of Novel Functional Molecules by Hybridization of Biomolecules with Transition Metal Clusters, Grant-in-Aid for Exploratory Research, 1 April 2007–31 March 2009.

Okazaki M, Design of Novel Catalysts Based on Redox-Active [4Fe–4C] Core, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2008–31 March 2010.

Okazaki M, Construction of Functional Molecules Based on Characteristics of Polymetallic Cores, Grant-in-Aid for Scientific Research (B), 1 April 2008–31 March 2012.

Takita R, Development of Catalytic Reactions Using Low Coordinate Phosphine Ligands, Grant-in-Aid for Young Scientists (Start-up), 1 August 2007–31 March 2009.

Nakajima Y, Precise Design of Rare-earth Metal Based Catalysts Directed to Development of Novel Olefin Polymerization Process, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2008–31 March 2010.

Award

Nakajima Y, Poster Prize ICOMCXXIII, Rennes, France, 14 July 2008.

Synthesis and Structures of Platinum(0) Alkyne Complexes with Extended π-Cojugated Systems

Organometallic complexes with extended π-conjugated systems have attracted continuous research interest because of their potential applications in material science. We recently found that 1,2-bis[(2,4,6-tri-*tert*-butylphenyl) phosphinidene]cyclobuta[*l*]phenanthrene (DPCB-phen) as a low-coordinated phosphorus ligand forms platinum(0) alkyne complexes with extended π-conjugated systems, [Pt(RCCR)(DPCB-phen)] [R = CO_2Me (**1a**), Ph (**1b**), C_6H_4-*p*-OMe (**1c**), C_6H_4-*p*-NMe_2 (**1d**)]. The colors of the complexes are highly dependent on alkyne ligands, showing a marked variation from reddish orange to teal.

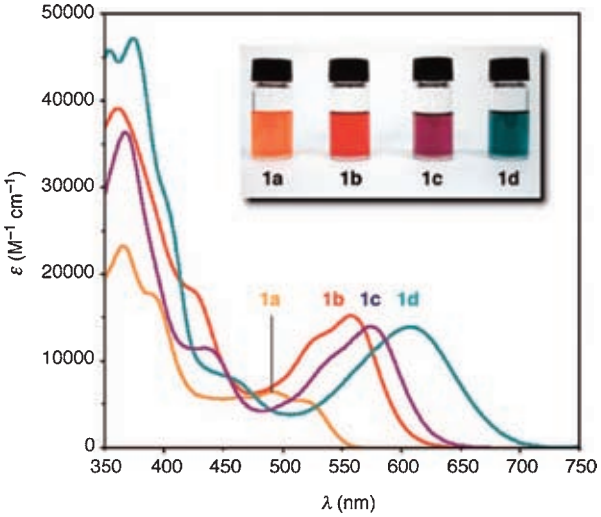


Figure 1. Absorption spectra of **1a-d** in $CHCl_3$.

Synthesis and Ligand Property of 1-Phosphaethenyl-2-phosphanylferrocenes

Novel bidentate-ligands with planar chirality, Fc (CH=PMes*)PAr_2 [Fc = ferrocene, Mes* = 2,4,6-tri-*tert*-buthylphenyl; PAr_2 = PPh_2 (**2a**), P(1-naphthyl)Ph (**2b**)], have been prepared for exploring the following points: (1) direct comparison of the ligand properties of phosphaalkene and phosphane, (2) application of phosphaalkene ligands to catalytic asymmetric reactions. Compounds **2a** and **2b** readily react with $[PtMe_2(\mu\text{-}SMe_2)]_2$ in Et_2O to afford dimethyl complexes with bidentate coordination of these ligands (**3a**, **3b**). The X-ray structure of **3b** indicates almost identical trans-influence of the phosphaethenyl and phosphanyl groups, showing comparable σ-donating abilities of those components. The complex [Pd(η^3-allyl)(**2a**)]OTf catalyzes hydroamination of 1,3-cyclohexadiene with aniline in toluene in the presence of molecular sieves 5A at room temperature, giving *N*-cyclohexen-3-ylaniline in 84% yield.

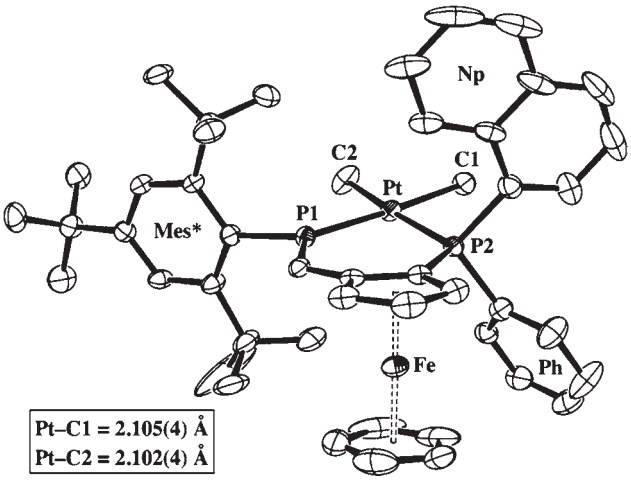
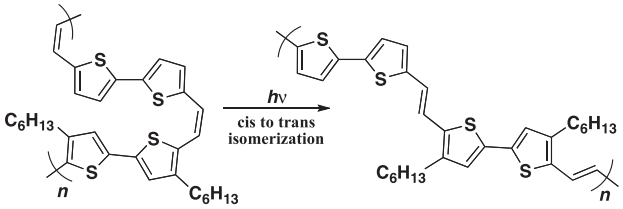


Figure 2. Molecular structure of **3b**. Hydrogen atoms are omitted for clarity.

Synthesis and Properties of All-cis Poly(arylene vinylene)s Containing Thiophene Cores

All-cis poly(arylene vinylene)s (PAV) containing thiophene units in the main chain have been prepared in highly stereocontrolled manner by Suzuki–Miyaura-type polycondensation. Thin films of all-cis PAVs, developed by spin-coating on quartz substrates, are insolubilized under UV-irradiation, along with cis–trans isomerization of the vinylene units. The photo-irradiated films exhibit relatively high carrier mobility up to 3.5×10^{-2} $cm^2/V{\cdot}s$, while the original films of all-cis PAVs are insulators.



Scheme 1. Photo-isomerization of all-cis poly(dithienylene vinylene).